

# SYNTHETIC ORGANIC CHEMICALS

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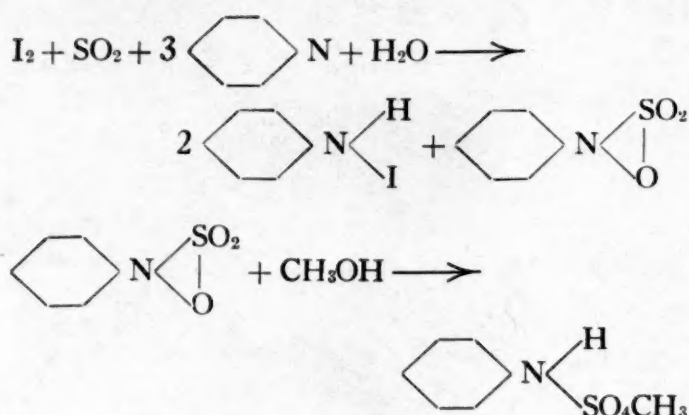
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## Titrimetric Procedures Using The Karl Fischer Reagent

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THE Karl Fischer method (1) for determining moisture makes use of a reagent consisting of sulfur dioxide, methanol, and iodine dissolved in pyridine. When this dark-colored solution is added to an organic solvent containing water, the brown color disappears, leaving a yellowish or red-colored solution, depending upon the age of the reagent, the nature of the organic solvent, and the amount of water in the solvent. When all the water in the titration mixture has reacted, the appearance of the brown color of the reagent serves as a visual end point.

It has been shown (2) that the chemical reaction occurs in two steps:



The second reaction does not involve water and hence all conditions must be controlled carefully during the titration

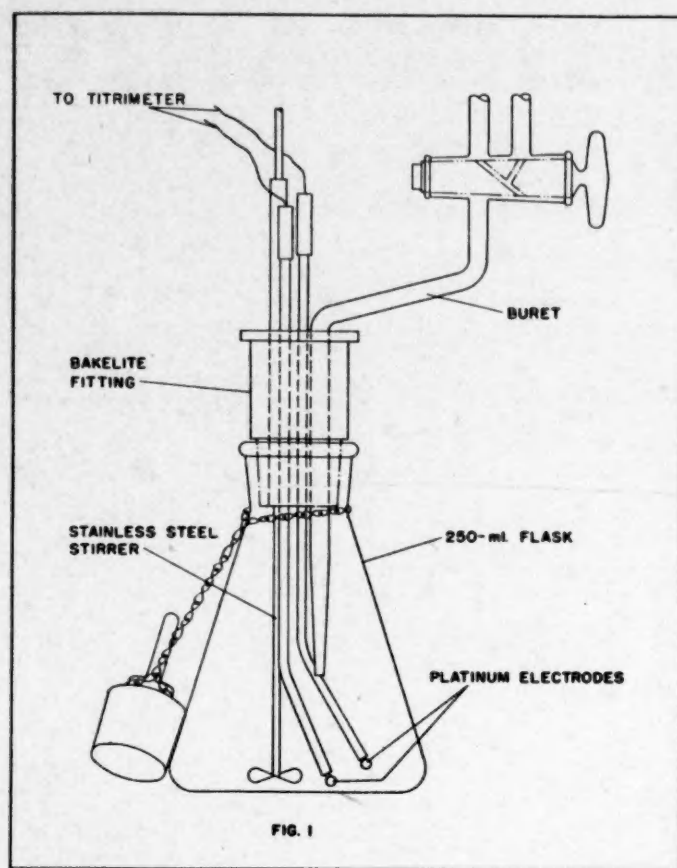
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in order to get reproducible results. There is no simple stoichiometric relation between the water consumed and the amount of Fischer reagent used up but this is not serious because the reagent can readily be standardized against pure water or a standard solution of water in some organic solvent.

The reagent has been used for determining water in liquids and solids, both organic and inorganic (3), and there are comparatively few interfering substances that cannot be removed in a simple manner. It is especially useful in analytical procedures that involve chemical reactions in which water is either eliminated or absorbed (3), (4), (5).

It is desirable to keep at a minimum the moisture content of the organic liquids used as solvents during the titration, and to dispense all solvents and reagents from apparatus that is well protected from atmospheric moisture. Methanol and ethanol are conveniently dehydrated, by means of metallic magnesium, to a moisture content of less than 0.01 per cent (7), (8).

The precision of the method is highest when an excess of the Karl Fischer reagent is added to the titration mixture containing water, in a closed vessel, and the excess then back-titrated with a standard solution of water in methanol,

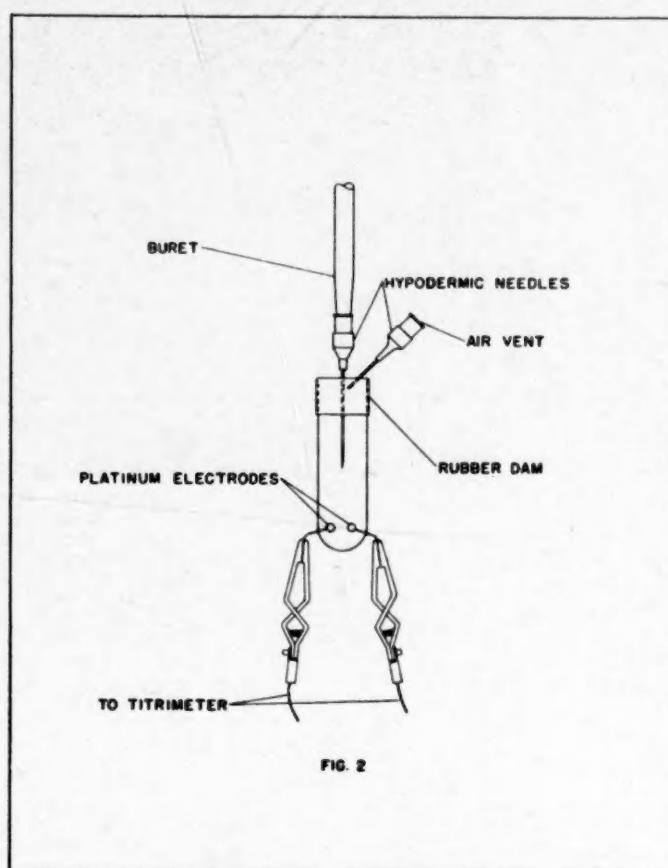


using an electrometric method of detecting the end point.

For titrations on a macro scale, where from 5 to 250 milligrams of water are to be titrated, an apparatus like that shown in Figure 1 is satisfactory (6). The buret tip, the stainless-steel stirrer, and the platinum electrodes are led through a Bakelite stopper turned to a standard taper that will fit a 250-ml. Erlenmeyer flask. The stirrer can be lifted when the flask is placed in the apparatus.

For micro-titrations, where from 0.5 to 50 milligrams of water are to be titrated, it is of greater importance to exclude atmospheric moisture. This can be done by sealing platinum electrodes permanently into a glass titration vessel which is covered with a rubber diaphragm (9). The solvents, liquid samples, and reagents are added through hypodermic needles, as shown in Figure 2. The solution is stirred by shaking the small titration vessel.

Atmospheric moisture can also be excluded satisfactorily by using a multiple-necked titration vessel with standard taper ground-glass joints, so that the stirrer, the electrodes, and the burets



can be interchanged quickly, thus admitting a minimum amount of atmospheric moisture (10).

The end point can be detected by the conventional potentiometric method, using a platinum-tungsten bimetallic electrode system combined with a vacuum-tube pH meter (11).

The manipulation difficulties are reduced somewhat if a polarized monometallic platinum electrode system is used with the so-called "dead-stop" apparatus (6), (10). The galvanometer of this apparatus is deflected completely off its scale when the polarized electrode system is in contact with excess Fischer reagent. During the titration of the reagent with standard water solution, the galvanometer remains deflected until the end point is approached. Near the end point the galvanometer is affected by each addition of water solution, and at the end point the galvanometer suddenly comes to a steady reading near its rest point.

The most satisfactory method of detecting the end point is the polarized monometallic platinum electrode system combined with a vacuum-tube titrim-



eter of the cathode-ray or "magic-eye" type (12). The titrimeter is adjusted so that the deflection angle of the cathode-ray tube is at a maximum when the electrode system is in contact with excess Fischer reagent. During the titration with standard water solution, the cathode-ray tube remains unchanged until the end point is approached. Near the end point, the deflection angle is affected by each addition of water solution, and

at the end point the deflection angle suddenly decreases to zero.

For the routine use of the Karl Fischer reagent, it is necessary to dispense all solvents and reagents from automatic dispensing apparatus well protected from atmospheric moisture. The test method will be more reliable when the titrations are made in a closed system, using an electrometric method to detect the end point.

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## A Streamlined Extractor

By F. P. PINGERT\*

THE standard Soxhlet extractor has certain drawbacks which limit its usefulness. The projecting siphon and vapor line are a nuisance. Aside from the fragility of this arrangement, the conventional apparatus shows other undesirable features. Because of the exposed construction of the chamber, the solvents cool off very rapidly, and this tends to slow down the process of extraction.

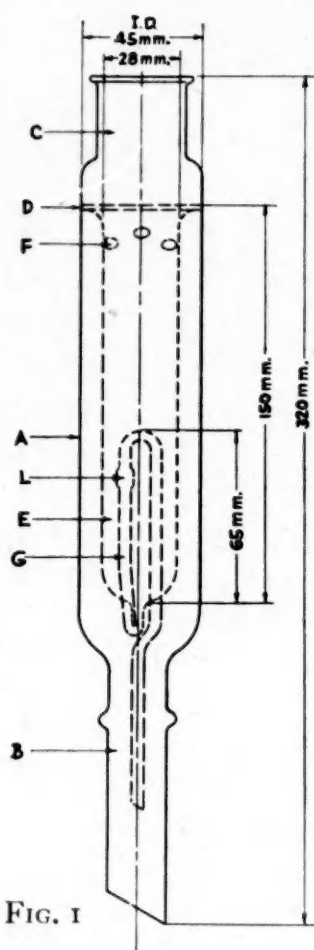


FIG. 1

The following streamlined version of the intermittent type of extractor avoids most of these difficulties. All of the working parts are enclosed in a jacket, *A* (Figure 1), whose stem, *B*, connects with the still pot, while its top, *C*, carries the condenser. By means of an inner seal at *D*, the extracting chamber, *E*, is firmly implanted in the barrel. Several holes, *F*, permit the passage of the solvent vapors to the condenser, *C*. The siphon, *G*, is simply a doubly bent tube which projects freely into the lumen of the jacket, *A*, and its stem, *B*. No inner seal is required to support the siphon, because it does not have to withstand any mechanical shock. The enlarged section, *L*, of the siphon tube serves to facilitate the escape of vapors. None of the dimensions of the apparatus are critical.

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They are limited only by incidental factors, such as the available sizes of paper extraction thimbles, etc. The dimensions in Figure 1 serve merely as an illustration.

When the apparatus is in use, it is advantageous to offset the paper extraction thimble from the bottom of the chamber, *E*, by means of a glass stage, porcelain chips, or similar material. (An old glass stopper serves very well.) This provides a "pool" where the extract may collect, and insures rapid drainage whenever the siphon starts.

No "vapor lock" is likely to be encountered when using this apparatus, provided ample hydrostatic head exists between the top of the siphon and the top of the thimble.

The speed of extraction is, on the average, double that obtainable in the standard apparatus, but a ten- to twentyfold increase in rate may be obtained

under favorable circumstances. This increase in the speed of extraction is partly due to a higher reflux rate and partly to the hotter solvent. In the conventional apparatus the cooled liquid which returns to the still pot interrupts the reflux until the lost heat is recovered. The extraction cycle of the streamlined apparatus is more rapid because it returns the extracts to the still pot at almost the boiling point and the ebullition is not affected appreciably. Thus, the extraction cycle is more rapid.

The over-all construction of the apparatus is no more complicated than that of a Soxhlet extractor and is reasonably free from strains. (A Soxhlet extractor contains two double seals, which require careful annealing.) The suggested extractor is sturdy and also simple to clean. Furthermore, it is easy to store when not in use.

## New Eastman Organic Chemicals

5631	2-Aminopyrimidine MP 126-127° $\text{NH}_2\text{C}:\text{NCH}:\text{CHCH}:\text{N}$ ...MW 95.10	100 g.	\$2.80 C
5587	Bicyclo [2,2,1] 5-heptene-2,3-dicarboxylic Anhydride.... $\text{CH}_2\text{CHCH}:\text{CHCHCHCH}(\text{CO})_2\text{O}$ ...MW 164.15	100 g.	7.50 C
T 5655	Cetyldimethylamine (Techn.) $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_2$ ...MW 269.50	500 g.	7.00 D
T 5638	$\alpha,\beta$ -Dichloroethyl Acetate (Techn.) $\text{CH}_3\text{COOCHClCH}_2\text{Cl}$ ...MW 157.00	500 g.	4.00 C
P 5639	Ethyl Chloroacetal (Pract.) 90% boiling at 153-157° $\text{CH}_2\text{ClCH}(\text{OC}_2\text{H}_5)_2$ ...MW 152.62	500 g.	5.00 D
P 5637	2-[ $\beta$ -Hydroxyethyl]pyridine (Pract.) 95% boiling at 113-115°/8mm. $\text{N}:\text{CHCH}:\text{CHCH}:\text{CCH}_2\text{CH}_2\text{OH}$ ...MW 123.15	500 g.	4.50 D
T 5652	Myristyldimethylamine (Techn.) $\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_2$ ...MW 241.45	500 g.	8.50 D
T 5656	Octadecyldimethylamine (Techn.) $\text{CH}_3(\text{CH}_2)_{17}\text{N}(\text{CH}_3)_2$ ...MW 297.55	500 g.	6.50 D
P 5474	1,3-Pentadiene (Pract.) BP 42-43° $\text{CH}_2:\text{CHCH}:\text{CHCH}_3$ ...MW 65.09	3 kg.	3.00 G
T 5664	Tetraethanolammonium Hydroxide (40%) (Techn.) $(\text{HOCH}_2\text{CH}_2)_4\text{NOH}$ ...MW 211.26	1 kg.	2.35 E